ISOPROPYL ALCOHOL AS A COAL LIQUEFACTION AGENT

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The use of Tetralin and similar H-donor solvents in the hydroconversion of coal to liquid fuels is well known (1), and is important in large-scale coal conversion processes (2). We present here evidence that isopropyl alcohol can act as an H-donor solvent, yielding products similar to those generated in Tetralin-based systems. Contrary to the case for Tetralin, it appears that the action of the isopropyl alcohol can be promoted by the presence of bases. This report presents initial data from a research program still in progress; a full account of the work will be presented in a subsequent manuscript.

EXPERIMENTAL PROCEDURES

The experiments described here were carried out in a 300-ml MagneDrive, stainless steel autoclave from Autoclave Engineers. The substrate was beneficiated Illinois No. 6 coal supplied by Pennsylvania State University (PSOC 26), and ground under nitrogen in a ball mill to -60 mesh. In each run, 5-g samples of the coal were used, in addition to 75 to 150 g of alcohol solvent. These experiments were run at $335^{\circ}C$ for 90 min, with typically 45 min heat-up and 60 min cool-down periods. No hydrogen was used in any of the experiments described, and the pressures are those generated by the solvents themselves. The reaction temperature of $335^{\circ}C$ was above the critical temperatures of the alcohols used.

In these experiments the product mixture was filtered, the residue washed with more solvent until the washings were colorless, and the filtrate recovered by evaporation of the solvent under vacuum. For those cases in which alkoxide salts were used, all fractions were appropriately neutralized with concentrated HCl. Both the filtrate and residue were then dried to constant weight at $110^{\circ}C$ under < 1 torr pressure. Mass balances were generally greater than 95%. In all cases the isolated filtrate was found to be fully pyridine-soluble. Pyridine solubilities of the residues were determined at room temperature, with 0.5 g of a product coal fraction stirred for 1 hr in 50 ml pyridine. The pyridine solubilities of the residues were established for all cases and recorded as the fraction of the residue soluble in pyridine. For some cases, it was convenient to refer to the composite pyridine solubilities and elemental composition values, that is, these values for the entire coal sample. In these instances the individual values for both the filtrates and residues were appropriately summed and recorded.

H_{al}/H_{ar} ratios were obtained from the proton NMR spectra, which were run on a Varian EM 360 spectrometer using nearly saturated solutions of sample in pyridine-d_5 or CS_2/pyridine-d_5 mixtures. The SRC used was supplied by Catalytic, Inc., Wilsonville, Alabama, sample number 16573, derived from an Illinois No. 6 coal and processed to K109 SRC specification.

RESULTS AND DISCUSSION

Autoclave Experiments

The results of a series of experiments run at 335°C with a number of solvents are summarized in Table 1. The figures for the pyridine solubilities and elemental analyses are composite values, calculated from the respective values for both the filtrate and residue from each run.

Table 1

TREATMENT OF BENEFICIATED ILLINOIS NO. 6 COAL

AT 335°C FOR 90 MINUTES[a]

Run No.	Conditions[b]	Pyridine[c] Solubility (%)	Elemental Analyses[d]			
			H/C (molar)	O/C (molar)	N (%)	S (%)
-	Untreated coal	17	0.79	0.117	1.58	2.20[e]
21	iPrOH (ρ = 0.5)	50	0.81	0.086	1.63	1.82
53	iPrOH + Al(OiPr)$_3$[f] (ρ = 0.3)	61	0.87	0.073	1.64	1.81
54	iPrOH + K(OiPr)[f] (ρ = 0.3)	97	0.95	0.090	1.69	0.71
62	iPrOH + K(OiPr)[g] (ρ = 0.3)	89	0.83	–	1.33	–
36	tBuOH (ρ = 0.2)	13	–	–	–	–
61	tBuOH + K(OtBu)[f] (ρ = 0.5)	12	–	–	–	–
48	Tetralin[h]	48	0.81	0.079	1.58	1.83

[a] No hydrogen is added to the system; the pressure during a run is in the range of 2000 psi, and due only to the vapor pressure of the medium. The starting coal has been beneficiated to about 2% ash.

[b] Since 335°C is above the T_c of both alcohols, the amount of solvent present is expressed as ρ, the number of g of alcohol per ml of reactor volume (285 ml).

[c] Solubility of recovered material in pyridine, based on ash free weight of the starting coal. Composite values, as discussed in the text.

[d] Ash-free basis. Composite values, as discussed in the text.

[e] This value represents the organic sulfur in the starting coal.

[f] 1 g metal alkoxide/5 g coal was used.

[g] 0.5 g potassium salt/5 g coal was used.

[h] The critical temperature of Tetralin is 484 ± 32°C. Thus the medium here was subcritical.

The table shows that the untreated coal has a pyridine solubility of 17%. In Run 21, in which the coal is treated with isopropyl alcohol, the resulting product coal displays a solubility in pyridine of 50%. This result is clearly significant, and is comparable to the results for a similar experiment with Tetralin, Run 48,

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where the resultant coal product shows a 47% pyridine solubility. The surprising similarity of the elemental analyses for the products in both cases leads us to conclude that, like Tetralin, isopropyl alcohol acts as an H-donor under these conditions.

An alternative possibility is the introduction of isopropyoxyl groups to the coal, which would possibly increase both the solubility and the H/C ratio. This route is most likely ruled out for Run 21, however, on the basis of the decrease in the O/C ratio with respect to the starting coal.
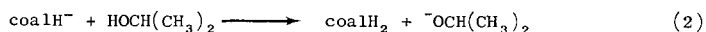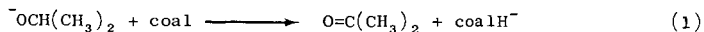
This point is confirmed by the results of Run 36, where t-butyl alcohol was used. The structural differences between isopropyl and t-butyl alcohols are insignificant for work at these temperatures, and if alkoxylation were important, it would take place with both alcohols. The pyridine solubility of the product coal from the t-butyl alcohol experiment, however, is somewhat less than that of the starting coal, and significantly less than the results for Runs 21 and 48. These data thus support our contention that for the isopropyl alcohol case no incorporation of solvent into the coal has taken place. On the other hand only the isopropyl alcohol can provide hydrogen, perhaps as hydride, as discussed below. The large difference in the results is thus consistent with H-donation by isopropyl alcohol.

These results suggest a similarity in general mechanism to the known Meerwein-Pondorff reduction of carbonyl groups with isopropoxide salts, most commonly aluminum isopropoxide in isopropyl alcohol (3). In this reaction hydride ion from the oxygen-bearing carbon in the alcohol is transferred to a carbonyl group, thereby reducing it. To test this possible mode of reaction, aluminum isopropoxide was added to the reaction mixture in Run 53 and potassium isopropoxide was added in Run 54.

For Run 53, the product is 61% soluble in pyridine, somewhat enhanced relative to the value for isopropyl alcohol alone. For the potassium isopropoxide case the result is striking. The product coal is essentially fully pyridine-soluble, and additionally, the organic sulfur in the coal has been reduced to the low value of 0.41%.

While these data strongly support a hydride transfer process, it might be proposed that the results were due to some kind of base-promoted dissolution. This possibility was eliminated by the data from Run 61, in which potassium t-butoxide in t-butyl alcohol was used. Here the result is little different from that for t-butyl alcohol alone.

Thus it can be concluded that isopropyl alcohol can act as an H-donor solvent for coal conversion in a process involving hydride transfer from the alcohol, or alkoxide salt, to the coal. The net transfer of H_2 to the coal could involve a a chain process, such as

$$^-OCH(CH_3)_2 + coal \longrightarrow O=C(CH_3)_2 + coalH^- \qquad (1)$$

$$coalH^- + HOCH(CH_3)_2 \longrightarrow coalH_2 + {}^-OCH(CH_3)_2 \qquad (2)$$

in which the alkoxide ion is regenerated with each cycle, H_2 has been transferred to the coal, and acetone is formed. The formation of acetone has in fact been confirmed qualitatively, and experiments are currently under way to assess the quantitative nature of the process.

Product Characterization

While we have written reaction (2) with the notation $coalH_2$, we do not wish to imply that simple hydroaddition to multiple bonds has necessarily occurred. The question of the specific site of hydrogen reaction remains open, and it is of interest to establish the degrees to which hydroaddition and hydrocracking have taken place.

Accordingly, it is convenient to look at our product data in more detail, namely in terms of the separated fractions of the product coal. Table 2 presents data for the fraction of the starting coal isolated from the solvent after reaction, the H/C and H_{al}/H_{ar} ratios for that fraction, the H/C ratio of the residue, and the solubility of the residue in pyridine. Also given are H_{al}/H_{ar} for the starting coal, for the residue from the potassium isoproxide experiment, and for an Illinois No. 6 SRC. The values for pyridine solubility of the residue are given as the fraction of the residue soluble in pyridine. For example for Run 21, of the starting 5 g of coal, 1.0 g, or 20%, was recovered from solution in isopropyl alcohol at the end of the run. Of the remaining 4.0 g of residue, 1.5 g, or 37.5% was soluble in pyridine.

Table 2

ILLINOIS NO. 6 COAL WITH VARIOUS MEDIA
AT 335° FOR 90 MINUTES

Run No.	Filtrate[a]				Residue		
	Medium	Fraction of Starting Coal[b] (%)	H/C	$\dfrac{H_{al}}{H_{ar}}$	H/C	$\dfrac{H_{al}}{H_{ar}}$	Pyridine Solubility[c] (%)
Untreated coal	-	-	-	-	0.79	5.2[d]	17.0
25	Heptane	1.7	1.20	3.2	0.79	-	6.9
48	Tetralin	17.5	0.95	2.2	0.79	-	35.8
21	i-Propyl alcohol	20.0	0.95	2.1	0.78	-	37.5
54	KOiPr/ i-propyl alcohol	40.0	1.08	3.4	0.87	1.8	95.0
SRC	-	-	-	-	0.75	1.2	99.0+

[a] The solubilities of the untreated coal in the media are ≤ 1% for all cases.

[b] These values represent the solubilities of the resultant coal products in the respective media. The filtrates were found to be completely pyridine soluble in all cases.

[c] These values represent the fraction of the isolated residue soluble in pyridine.

[d] G. Hill, H. Hariri, R. Reed, and L. Anderson, Advances in Chemistry Series 55, 427 (1966).

Results for an experiment with heptane (Run 25) are presented in the table for comparison. Clearly the heptane run did not result in much coal dissolution, nor did the residue display any unusual behavior.

For Runs 48 and 21, however, with Tetralin and isopropyl alcohol, respectively, about a fifth of the starting coal is converted to material soluble in the media themselves, and the H/C ratios are enhanced. The residues for both cases have also undergone chemical change. For both the Tetralin and the alcohol experiments the residues are 35-40% pyridine-soluble. The H/C values for these fractions, however, are essentially the same as that for the starting coal. Thus it would appear that, for both solvents, a chemical process is taking place that (1) adds hydrogen to some fraction of the coal, converting it to material soluble in the respective media, and (2) generates a residue with a large pyridine solubility, but with no significant increase in hydrogen content.

The results for Run 54 with potassium isopropoxide show that 40% of the starting coal is converted to a product soluble in the reaction medium. That fraction is considerably enriched in hydrogen, and a substantial fraction of the added hydrogen is aliphatic, comparable to the small quantity of material isolated from the filtrate of the heptane experiment. The residue in this case is essentially fully pyridine-soluble and, in contrast to those for Runs 21 and 48, has been enriched in hydrogen. The H/C and H_{al}/H_{ar} data are reasonably similar to those shown in the table for SRC, although it is clear that our product has more overall aliphatic character than the SRC. Both are also considerably more aromatic in character than the starting coal, although the H_{al}/H_{ar} value for the coal is for an "average coal" and is probably only a rough, semiquantitative value of the ratio for our starting coal.

If just the hydrogen and carbon contents are considered, the values for both the Run 54 residue and the SRC permit the calculation of an average molecule for both. Interestingly, the data for both can be accommodated by

$$C_{90}H_{ar31}H_{al37}(CH_{al2})_{10}$$

$$\underbrace{\hspace{3cm}}_{\text{SRC}} \underbrace{\hspace{3cm}}$$

residue, Run 54
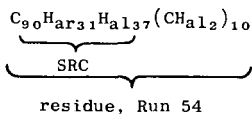
This result includes number average molecular weight data in the range 1000-1300, which we have obtained for both materials. It appears that the two may be simply related, with additional polymethylene bridges, or hydroaromatic components, present in our product. The implications of this result await further study.

REFERENCES

1. M. Orchin and H. Storch, I & EC, $\underline{40}$, 1385 (1948).

2. See, for example, L. Furlong, E. Effron, L. Vernon, and E. Wilson, "Coal Lique-faction by the Exxon Donor Solvent Process", presented at the 1975 AICHe Meeting, Los Angeles, California, November 18, 1975.

3. A. Wilds, Organic Reactions, $\underline{2}$, 181 (1947).